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9**catalyst-free production of biodiesel from Ceiba pentandra (kapok) oil with high free fatty acid contents Lu Ki** Onga,1, **Chintya** Effendia,1, **Alfin** Kurniawana,1, **Chun Xiang** Linb, **Xiu Song** Zhaob,**, **Suryadi**

Ismadjia,* a

2**Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia** b **School of Chemical Engineering, The University of Queensland, St. Lucia,** Brisbane, **QLD 4072, Australia article info Article history: Received** 27 November 2012 **Received in revised form** 29 March 2013 **Accepted** 31 May 2013 **Available online** 28 June 2013 **Keywords:**

Supercritical transesterification Methyl ester Statistical design Response plot abstract Catalyst-free

15**biodiesel production from** non-edible **Ceiba pentandra** (kapok) **oil**

via supercritical methanol transesterification was demonstrated in this work. The supercritical transesterification experiments were performed in a batch reactor at temperatures of 250e350 C, pressures of 10e18 MPa, reaction times of 120e600 s, and methanol to oil molar ratios of 15:1e35:1. Response surface methodology (RSM) and four-way analysis of variance (ANOVA) were applied for the design and optimization of the experiments with respect to temperature, pressure,

19**reaction time, and molar ratio of methanol to oil** simultaneously. **The**

response (i.e., FAME yield)

13**was fitted by a quadratic polynomial regression model using least square analysis in a five-level-four-factor central composite design (CCD). The**

optimum conditions were found as follows:

6**methanol to oil molar ratio of** 30 **:1, temperature of** 322 **C,** pressure **of**

16.7 MPa, and reaction time of 476 s with FAME

8**(fatty acid methyl ester) yield of**

95.5%. The significance of the reaction parameters toward FAME yield was in the order of methanol to oil molar ratio > reaction time > pressure > temperature. Ó 2013 Elsevier Ltd. All rights reserved. 1. Introduction The compliance of energy demands for transportation and industrialization purposes in most countries still relies on the fossil fuel sources. However, fossil fuels are non-renewable energy sources and will be totally depleted in the near future. Furthermore, the engine emissions produced

4**from the** combustion **of fossil fuels** contain high **amounts of**

air pollutants therefore raising environ- mental concerns. Biodiesel (BD) has been highlighted as an attractive renewable fuel for addressing the issues concerning non-sustainable petro-diesel sources and environmental awareness in the society. Compared with petrol-diesel fuel, biodiesel is more environmentally friendly due to low emitted air pollutants (e.g., unburned hydro- carbons, NOx, COx, and particulate matters) from its combustion. Furthermore, it is biodegradable, less toxic, safe for handling and storage, has excellent lubricity, and provides energy density similar to conventional petro-diesel therefore it can be directly used without * Corresponding author. Tel.: þ62 31 389 1264; fax: þ62 31 289 1267. **

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11**0360-5442/$ e see front matter Ó 2013 Elsevier Ltd. All rights reserved.**
http://dx.doi.org/10.1016/j.energy.2013.05.

069 any modifications of engine and refueling station [1]. Because of some benefits of biodiesel in conjunction with its renewability, sustainability, and environmental friendliness, the developments of this liquid fuel as a substitute for petro-diesel are moving rapidly. Several technologies are available for biodiesel production such as microemulsion [2], direct use and blending of diesel/oil [3], thermal cracking (pyrolysis) [4], and transesterification (alcohol- ysis) [5]. Among them, the most popularly used method is trans-esterification

4**in the presence of** a **catalyst (e.g.,** liquid acids **or**

bases, enzymes, or solid catalysts). Endalew et al. developed various metal oxides doped with alkali metal (i.e., lithium) or rare earth metal (i.e., lanthanum) as heterogeneous

15**catalysts for the trans- esterification of** FFA-rich **jatropha oil**

in a single-step reaction [6]. A similar work has been conducted by Jain and Sharma to prepare biodiesel from crude jatropha oil via

15**a two-step catalyzed** trans- **esterification process**

[7]. Two kinds of catalysts were used namely sulfuric acid in the pretreatment step and sodium hydroxide in the subsequent process. Meng and colleagues have studied NaOH- catalyzed transesterification

19**for the production of biodiesel from** treated **waste cooking oil**

[8]. They found that the catalyst con- centration of 1 wt% gave maximum conversion efficiency under mild operating condition. The feasibility of the base-catalyzed biodiesel production from palm cooking oil and waste frying oil has been evaluated by Peng-Lim et al. [9] and Uzun et al. [10], respectively. However, the catalytic biodiesel production has several drawbacks such as time-consuming due to low reaction rate and corrosion risk for acid-catalyzed; high sensitivity to free fatty acid (FFA) and water contents in the oil

feedstock and difficulty in the separation of biodiesel and catalyst from soap for alkaline catalyst; high cost and deactivation risk of the active sites for both enzyme and heterogeneous catalysts. Moreover, biodiesel produc- tion employing liquid catalysts requires complex and costly treat- ments for the acidic or alkaline wastewater. Recently, the catalyst- free technique for biodiesel production has been considered to be able to mitigate the drawbacks of catalytic biodiesel production from both technical and environmental viewpoints. Supercritical transesterification (SC-TE) has proven as an attractive technique for high yield and high purity biodiesel production without involving any catalyst and generating toxic wastewater [11,12]. Other advantages of this route include fast reaction kinetics, ease separation of products, and tolerance to

37**FFA and water contents in the** oil **feedstock**

because esterification of free fatty acid (FFA) and transesterification of triglycerides proceed simultaneously [12]. Indonesia is a tropical country that has abundant natural resources from the plantation, agriculture, marine, or forestry sectors. Among these, kapok (Ceiba pentandra) tree, also known as silk-cotton tree, is a tall plant from Malvaceae family that widely distributed in the tropical rainforests. Some parts of this plant are of high economic value used as timber and pod. Kapok pod comprises of fiber (about 17%) that is primarily utilized in making pillows and mattresses while the resulting seeds end merely as a waste. The seed contains a fairly high non-edible oil (about 40 wt%, dry basis) and therefore can be utilized as a potential biomass feedstock for biodiesel production. The production of kapok oil (KSO) in Indonesia reaches 15,000 tons in 2010 and sixty percents of them can be found in Java regions. In addition, the cultivation technique of kapok plant is quite simple with relatively short harvesting time (every 4e5 months) hence ensuring its feasibility as a sustainable biomass feedstock for the large-scale production of biodiesel. The studies about

12**biodiesel production from** kapok **oil via alkali- catalyzed**

transesterification have been recently reported in the lit- eratures [13,14]. In the present work, we conduct catalyst-free one- step transesterification of FFA-rich kapok oil to biodiesel with supercritical methanol as the reacting alcohol. So far, there is no report available about the transesterification of kapok oil to biodiesel via a non-catalytic route. Besides, the application of one-step supercritical transesterification for biodiesel production still rarely reported, particularly using low grade or unrefined oil feedstock. In this case, the most frequent technique used is through a two-step process viz. hydrolysis of fatty acid esters using sub/supercritical water, followed by supercritical methyl/ethyl esterification of fatty acids into methyl/ ethyl esters. For example, Minami and Saka [15], Kusdiana and Saka [16], and Ilham and Saka [17] firstly treated triglycerides in oils/fats in subcritical water for the hydrolysis reaction to produce fatty acids and these fatty acids are further converted to methyl esters through su- percritical esterification. They reported that by applying two-step process above, the reaction can be conducted at more convenient conditions and the backward reaction between glycerol and fatty acid methyl ester can be suppressed. In the case of one-step supercritical transesterification process, the most commonly used feedstocks are purified vegetable oils containing low free fatty acids (less than 1%), as employed by Gui et al. [18] and Tan et al. [19,20].

3**With regards to** statistical **design and optimization of supercritical**

transesterification process, most of previous studies only emphasize three experimental parameters. For example, Gui et al. [19], Tan et al. [20], and Patil et al. [21] deal with optimization studies of tempera- ture, reaction time, and

37**alcohol to oil molar ratio of the catalyst-**

free

4**biodiesel production from** purified **palm oil and**

Nannochloropsis sp. wet algae, respectively. Another study conducted by Sawangkeaw et al. [22] also focuses on the statistical design of supercritical meth- anol transesterification of refined palm kernel oil (PKO) to obtain a reliable three-parameter model for the process optimization with respect to temperature, pressure, and methanol/oil molar ratio. However, it should be recognized that at least four key parameters are needed to be statistically analyzed and optimized for the industrial process operation of supercritical-based biodiesel production. The alcohol to oil molar ratio and reaction time may be of relevance to the efficiency and economic aspects of the process while pressure and temperature may be associated with the design of high-pressure reactor system. Given this, the design of experiment and optimiza- tion of supercritical methanol transesterification of kapok oil into biodiesel in this work was conducted by incorporating four

16**reaction parameters** namely **methanol** to **oil molar ratio,** temperature, pressure, **and reaction time**

using response surface methodology (RSM) and four-way analysis of variance (ANOVA).

3**To this end, the present work provides** an insight regarding **the**

non-catalytic production of biodiesel from non-edible and underutilized kapok oil, which is not only opened a broader strategy to overcome the depletion of crude oil reserves worldwide, specifically in Indonesia country but also enriching the state-of-the-art in biodiesel research field. 2. Experimental sections 2.1. Materials Kapok oil was obtained from Subali Makmur Co., Ltd located in Pati, Central Java and used without further treatment. The acid value of the oil was determined by titration against standardized 0.25 M KOH solution by following ASTM D5555-95 test method [23] and found to be 19.84 mg KOH/g oil. The water content in the oil was analyzed on a Mettler-Toledo V20 compact volumetric KF titrator and found to be 0.02%. The fatty acids

25**composition of** kapok **oil was analyzed** on **a Shimadzu GC-**

2014

30**equipped with a flame** ionization **detector (FID) and a** Restek Rtx-65TG **fused silica capil- lary column (30 m 0.** 25 **mm**

0.10 mm). Helium (99.99%)

10**was used as the carrier gas at a** column **flow of** 40 **ml/min. The injection volume was 1 ml with a split ratio of** 1:40. **The**

temperatures of the injector and detector were operated at 365 C. The temperature of column oven was initially programmed at 50 C

22**for 1 min,** elevated **to** 350 **C at** 50 **C/min,** ramped **to** 365 **C at** 1 **C/min, and held for** 5 **min. The**

results are shown in Fig. 1. Methanol (99.8%, A.R. Grade) and anhydrous heptane (99%, A.R. Grade) were purchased from Merck, Germany. Methyl palmitate, 60 50 40

40**wt% 30 20 10 0 C16:0 C18:0 C18:1 C18:2 C20:0**

4**Fatty Acid** Compositions **Fig.** 1. **Fatty acid** compositions **of**

kapok oil

21**(C16:0 ¼ palmitic acid, C18:0 ¼ stearic acid, C18:1 ¼ oleic acid, C18:2 ¼ linoleic acid; C20:1** ¼ gadoleic **acid).**

27**methyl stearate, methyl oleate,** methyl linoleate, **and methyl** arachidate **with** a **purity** of **99%**

were supplied by Sigma Aldrich, Singapore and used without further purification. These compounds were used as the reference standards for the determination of FAME yield. Methyl heptadecanoate (99.5%, Fluka)

23**was used as** an **internal standard** in the **analysis of FAME** contents. **2.2.**

Supercritical transesterification (SC-TE) experiments The supercritical methanol transesterification experiments were performed in a 50 ml high pressure batch reactor. The reactor was custom-made by a local company from 316SS-grade stainless steel and equipped with a K-type thermocouple, a pressure gauge, and an external electric heater. The maximum working pressure and temperature of the system are 30 MPa and 400 C, respectively. The reactor was also connected to a nitrogen cylinder (15 MPa, 99.99%) and reciprocating horizontal piston-pump was used to introduce pressurized nitrogen to the system. The reaction operating procedure was described as follows: A known amount of methanol and KSO was loaded to the reactor to give a methanol/oil molar ratio of 15:1, 20:1, 25:1, 30:1, and 35:1. The reactor was purged with a certain amount of nitrogen to remove air and build-up some pressure in the reactor prior to heating. The methanol/KSO mixture was then heated from room temperature to desired reaction temperatures (250 C, 275 C, 300 C, 325 C, and 350 C) at a heating rate of 20 C/min. The temperature was controlled within 2 C and pressure was monitored by a pressure gauge in order to maintain isothermal and isobar reaction condi- tions.

34**Zero reaction time was** defined **when the temperature** and pressure in **the** system **reached the**

set values. After zero reaction time reached, the mixture was stirred by a magnetic bar at 500 rpm for a prescribed time (120 s, 240 s, 360 s, 480 s, and 600 s). Subse- quently, the reactor was rapidly cooled to room temperature and the mixture was removed from the vessel. The mixture was placed in a separation funnel for the phase separation between methyl ester and glycerol. The top phase (methyl ester) was taken and the residual methanol was vacuum-evaporated using an IKAÒ RV-10 rotavapor at 100 C for 1 h. The purified product was then subjected to gas chromatography analysis for FAME contents assay. 2.3. Analysis of FAME contents The FAME contents in the product were analyzed on a Shimadzu GC-2014 equipped with a FID and an Agilent narrowbore DB-Wax capillary column (30 m 0.25 mm 0.25 mm) as the stationary phase. Prior to injection, the sample was filtered using

34**a 0.22 mm PVDF syringe**

filter membrane and diluted in heptane. A given amount of 0.1 g/ml methyl heptadecanoate solution was added to the sample. The as-prepared sample was taken using a micro- syringe (1 ml) and injected into the column in a splitless mode. The

3**analysis conditions were** provided **in detail as follows: carrier gas ¼ helium at a constant linear velocity of**

40 cm/s; FID temperature ¼ 300 C; injector temperature ¼ 250 C; oven temperature ¼ 50

31**C for** 2 **min, ramped to 250 C at** 10 **C/min and held at 250 C for** 8 **min.**

Identification of methyl ester peaks in the samples was conducted by comparing retention time with the reference standards.

35**The yield** percentage **of fatty acid methyl** es- ters (wt%) **in the**

product was calculated by the following equation: P FAME ðwt%Þ ¼ 100 AME Aint VintCint Aint m (1) P where AME

17**is the total** peak **area of methyl esters,** Aint **is the peak area of** methyl heptadecanoate **internal standard,** Vint **is the** volume **of internal standard solution**

added to the

33**sample (ml),** Cint **is the concentration of** internal standard **solution (g/ml), and m is the mass of** the **sample (g).**

2.4. Characterizations of biodiesel fuel properties The fuel properties of biodiesel were characterized in terms of cetane index, flash point, cloud point, acid value, relative density, and kinematic viscosity. The results were compared with ASTM standard for biodiesel (ASTM D6751 [24]). All analyses were per- formed based on the standard test method as described in ASTM D613 for cetane index [25], ASTM D93 for flash point [26], ASTM D97 for pour point [27], ASTM D664 for acid value [28], ASTM D1480 for relative density [29], and ASTM D445 for kinematic viscosity [30]. 2.5. Statistical design of the experiments and process optimization Statistical design and process optimization of the experiments were performed by response surface methodology (RSM) and four- way analysis of variance (ANOVA) using Minitab software (Version 16.2.1). The optimized reaction parameters were

12**methanol to oil** molar ratio, **temperature,** pressure, **and reaction time. The** encoded parameters **and**

corresponding levels used in the experimental design are listed in Table 1. The choice of the factor levels of pres- sure and temperature used in this experimental design is based on the critical point of the reacting alcohol in which higher pressure and temperature above the critical pressure and critical tempera- ture of methanol are both required to induce the formation of supercritical methanol in the system. The experiments were per- formed in randomized order and after the completion of all experimental runs, the responses (i.e. FAME yield) were fitted with a quadratic polynomial regression model using least square anal- ysis. For reproducibility test, all data points were triplicated with their averages used as the result while the central data point (0,0,0,0) was replicated seven times and represented as a single data for each experiment. 3. Results and discussion 3.1. Effects of reaction parameters 3.1.1.

26**Methanol to oil molar ratio** Stoichiometrically, **methanol to oil molar ratio** of 3:1 **is**

required to form three moles of fatty acid methyl esters (biodiesel) and one mole of glycerol. In supercritical transesterification process, the molar ratio of methanol to oil used is significantly higher than stoichiometric amount. This can be explained on the basis that a large excess

24**molar ratio of** methanol **to oil is required to** bring **the reaction**

system to supercritical state. Moreover, a large excess molar ratio of methanol to oil was purposely used to drive the chemical equilibrium to the right-hand side based on Le Chatelier's principle and ensures high conversion of triglycerides within short time. The

32**conversion of triglycerides into fatty acid methyl esters** Table 1 **The**

encoded parameters and their corresponding levels used in the design of experiments. Reaction parameter Encoded factor Factor levels 2 1 0 1 2 Pressure (MPa) Time (s)

7**Temperature (C) Methanol to oil molar ratio X**

1 10 X2 120 X3 250 X 4 15:1 12 14 240 360 275 300 20:1 25:1 16 480 325 30:1 18 600 350 35:1 takes place sequentially as follows [31]: (i) the reaction between

29**methoxide anion** and **the carbonyl carbon of**

triglyceride to form methyl ester and diglyceride; (ii) the reaction between

29**methoxide anion** and **the carbonyl carbon of**

diglyceride to form methyl ester and monoglyceride; and (iii) the reaction between

29**methoxide anion** and **the carbonyl carbon of**

monoglyceride to form methyl ester and glycerol. Besides transesterification of triglycerides into methyl esters as the main reaction, some side reactions might also occur [32,33]: (1) hydrolysis of triglycerides

41**to produce fatty acids and glycerol;** (2) **esterification of fatty acids to produce** methyl esters **and water; and**

(3) glycerolemethanol reactions that associated with thermal degradation and etherification (or methanolysis) to produce ether- and/or ester-based oxygenated compounds and water. In the early period of the process (heating period), the reaction extent of esterification was limited due to poor miscibility of methanol in the oil; consequently this reaction mainly took place at the interface area between methanol and oil. Poor miscibility of methanol in the oil might also due to the minor concentration of methyl esters in the triglyceride phase [34]. Since the initial water content in KSO is fairly small (about 0.02%) and the rate of esterification reaction is restricted, the hydrolysis of triglycerides and glycerolemethanol reactions may not feasible to occur. Therefore, it can be concluded that esterification reaction acts as the promoter for other side re- actions. Additionally, it can be confirmed that the triglyceride contents in the oil feedstock are essentially unchanged and the resulting methyl esters from esterification of fatty acids can be ignored during heating period. With increasing temperature and pressure in the system, the mixture of methanol-oil becomes more homogeneous. Accordingly, the reaction extent of esterification becomes greater thereby water molecules are starting to accumulate in the system. This phenom- enon would make some amounts of triglyceride and methanol are not available for transesterification reaction due to partial hydro- lysis of triglyceride and glycerolemethanol side reactions, hinder- ing the formation of fatty acid methyl esters. Since a large excess of methanol existed and both hydrolysis and glycerolemethanol reactions occur in lesser extents than transesterification, it can be implied that the formation of methyl esters in the system still predominant, favoring high yield biodiesel production. Fig. 2a shows

28**the effect of methanol to oil** molar **ratio** toward **the** experimental **FAME yield**

at a constant pressure (14 MPa) and temperature (300 C) for reaction time of 120e600 s. From this figure, it can be seen an increase in FAME yield about 2.5-fold by increasing methanol to oil molar ratio from 15:1 to 30:1 regardless the effect of reaction time. At higher

8**methanol to oil molar ratio, the** contact between oil **and**

methanol molecules becomes more frequent hence higher conversion of triglycerides into FAMEs. A further

24**increase in methanol/oil molar ratio to** 35 **:1**

would lead to an insignificant change in FAME yield as compared to that obtained at a methanol/oil molar ratio of 30:1 throughout reaction time in this work, revealing the saturation miscibility condition of super- critical methanol in the oil phase at an applied temperature and pressure. Accordingly, supercritical methanol and oil cannot form more homogenous mixture beyond a molar ratio of 30:1 therefore leaving the excess reactant species (supercritical methanol that not reacted with triglyceride) in the mixture. The unreacted super- critical methanol would undergo glycerolemethanol reactions to form oxygenated compounds with ether and/or ester-based func- tional groups that can be used as biodiesel additives to improve the

combustion quality [35]. 3.1.2. Temperature and pressure Temperature and pressure are both regarded as the critical pa- rameters in the supercritical transesterification process because these parameters tune the density and solubility of the fluid at supercritical state. The

> 35**effects of temperature and pressure on the** supercritical methanol **transesterification**

of KSO were studied

> 38**at temperatures ranging from 250 C to** 350 **C and pressures from** 10 **MPa to** 18 **MPa** while maintaining **a**

> 8**methanol to oil molar ratio** at 25 **:1. The** use **of** high temperature in **the**

supercritical trans- esterification process can be explained by considering that thermal energy is

> 4**required for** inducing **the phase** transition **of** methanol **from liquid to** supercritical **phase.**

The critical pressure (Pc) and critical temperature (Tc) of methanol are 7.85 MPa and 240 C, respectively. This phase transition is an endothermic process therefore thermal energy is initially applied for the vaporization of methanol by overcoming liquid's chemical potential (i.e. intermo- lecular forces) and further used to raise temperature of methanol vapor surpassing its critical temperature. Moreover, high temper- ature may render a weakening effect on the hydrogen bonding of hydroxyl group in methanol, decreasing its dielectric constant and increasing its miscibility in the oil. In other hand, the phase tran- sition of liquid oil to supercritical state may not be observed due to high boiling point of triglyceride moieties thereby thermal energy supplied to the system is used for the partial vaporization of oil. The effects of temperatures and pressures on FAME yield are given in Fig. 2b and c, respectively. From these figures, it can be seen similar trends of experimental results, that is higher FAME yields at elevated temperatures and pressures. As shown in Fig. 2b, the yield of FAME was about 55% at 250 C and it was increased progressively to the highest point of about 90% by increasing temperature from 250 C to 350 C and lengthening transesterification time from 120 s to 600 s at a constant pressure of 14 MPa and methanol to oil Fig. 2. Experimental trends of FAME yield as a combined interaction between reaction time and

> 7**methanol to oil molar ratio** (a), temperature **(b), and** pressure **(c).**

molar ratio of 25:1. Increasing temperature above 350 C would lead to partial thermal degradation

> 32**of mono- and** polyunsaturated **fatty acid methyl esters** in **the**

mixture such as methyl stearate, methyl oleate, and methyl linoleate, as reported previously by Shin et al. [36]. Therefore, temperature of 350 C was selected as the maximum point for supercritical methanol transesterification of KSO in this work. Similar results are found in Fig. 2c in which the conversion of triglycerides into FAMEs enlarges with the increase of pressure and reaction time at a constant temperature of 300 C and methanol to oil molar ratio of 25:1. At higher pressure, super- critical methanol in the system becomes denser and its solubility (or solvation strength) in the oil increased. Accordingly, super- critical methanol and oil form more homogeneous mixture at higher reaction pressures thus facilitating transesterification of triglycerides into methyl esters. 3.1.3. Reaction time The effect of reaction time was investigated by conducting the experiments at different periods of time from 120 s to 600 s. Fig. 2aec displays the 3D plot of reaction time and FAME yield with incorporation of another reaction parameter. In these figures, it can be seen a gradual increase in FAME yield by extending reaction time from 120 s to 600 s. It is obvious that the prolonged reaction time allows a longer contact between oil and supercritical methanol in the mixture thereby larger portions of triglycerides and free fatty acids are converted to fatty acid methyl esters through trans- esterification and esterification reactions, respectively. 3.2. Statistical analysis and process optimization Biodiesel production via supercritical alcohol transesterification method requires large excess of reactant and is an energy-intensive process because of high pressure and temperature involving in the process. Therefore, the statistical analysis and process optimization are both crucial importance for economic consideration in the in- dustrial process operation. In this work, RSM was applied for determining the optimum reaction conditions for supercritical methanol transesterification of KSO that incorporates

7**methanol to oil molar ratio,** temperature, pressure, **and reaction time**

simulta- neously. A central composite design (CCD) with five-level-four- factor was used to design the reaction parameters and FAME yield as the response and the results are presented in Table 2.

14**A second-order** (quadratic) **polynomial** regression **model was employed to fit the response**

using least square analysis. The mathematical expression of the quadratic polynomial model is given as follows: Y ¼ k0þ kiXiþ X4 X4X4 kijXiXj (2)

14**i¼1 i¼1 j¼1 where Y is the response,**

k0, ki, and kij are the regression coefficients, Xi and Xj are the design parameters. The response plots were con- structed from the fitted model by using Minitab software (Version 16.2.1) and the results are displayed in Fig. 3AeF. The multiple regression coefficients of the model obtained by least square fitting are tabulated in Table 3. From this table, it can be noted that all linear and quadratic and interaction model terms of X1 * X2 and X2 * X3 are found to be crucial in maximizing FAME yield with p-values (calculated probability) less than the significance level (a-level) of 0.05. The adjusted coefficient of determination ðR2adjÞ for the fitted model was 0.94, which means that 94% of the total variance investigated was attributed by reaction

parameters. By inserting the fitted values of the regression coefficients (Table 3) Table 2 Central composite design for the response and corresponding parameters. Experimental Reaction conditions FAME yield (%) run X1 X2 X3 X4 1 1 2 1 3 0 4 1 5 1 6 0 7 1 8 0 9 1 10 1 11 1 12 0 13 0 14 1 15 0 16 2 17 1 18 1 19 1 20 1 21 1 22 1 23 1 24 0 25 0 26 2 27 0 28 0 29 0 30 0 31 0 1 1 1 1 0 0 1 1 1 1 0 0 1 1 0 2 1 1 1 1 1 1 0 0 0 0 1 1 0 0 0 0 1 1 1 1 1 1 1 1 1 1 1 1 1 1 2 0 0 2 0 0 0 0 0 0 2 0 0 0 0 0 1 69.8 1 52.8 0 63.9 1 65.5 1 64.5 0 65.2 1 65.3 0 75.8 1 78.3 1 59.4 1 48.6 0 63.2 2 67.4 1 64.4 0 63.8 0 75.7 1 52.7 1 54.6 1 79.7 1 79.8 1 95.5 1 57.2 1 66.6 0 58.6 0 58.3 0 58.7 0 64.2 0 63.4 0 78.7 0 63.8 2 28.3 into Eq. (2), the following quadratic polynomial model for the calculation of FAME yield is obtained: Y ¼ 63:9286 þ 4:3792X1 þ 6:5042X2 þ 4:4625X3 þ 7:6208X4 þ 1:3564X12 þ 1:7189X22 1:3189X32 3:4811X42 þ 2:0938X1*X2 þ 0:3312X1*X3 þ 0:4437X1*X4 þ 2:1062X2*X3 þ 0:6938X2*X4 þ 0:4313X3*X4 The profiles of the calculated FAME yield with incorporation of two design parameters are represented as surface response plots in Fig. 3AeF. Fig. 3A describes the effects of pressure (X1) and reaction time (X2) for maximizing

28**FAME yield. It can be seen the** significance **of**

both parameters toward FAME yield at the highest level (i.e. P ¼ 18 MPa and t ¼ 600 s) as the curvature lines of pressure vs. FAME and time vs. FAME rise sharply by changing the levels of one parameter from the lowest to the highest while keeping another parameter in the highest point. This observation is consistent with experimental results (Fig. 2c), that is higher FAME yields at higher pressure and longer reaction time. How- ever, the calculated FAME yield in this response plot can exceed 100%, indicating some errors due to the limitation of regression analysis by Minitab software that associated with two-parameter interaction at the highest level and/or less appropriate fitted values of the regression coefficients for interaction terms of X1 * X3, X1 * X4, X2 * X4, and X3 * X4 since the p-values of these terms exceeded the significance level. Similar results were observed in Fig. 3B that represents the two-parameter correlation between reaction time (X2) and methanol/oil molar ratio (X4) against FAME yield at constant pressure and temperature. As shown in this figure, lengthening transesterification time from 120 s to 600 s for methanol to oil molar ratios of 15:1e35:1 is responsible in Fig. 3. Response surface plots of FAME yield with two design parameters interaction. maximizing FAME yield. Meanwhile, FAME yield was hardly affected by the increasing levels of molar ratio of methanol to oil from 0 (25:1) to 2 (35:1) regardless the change in reaction time. This may indicate that the formation of fatty acid methyl esters is Table 3 The fitted values of the multiple regression coefficients for the calculation of FAME yield. Term Coefficient SE coefficient T p (a ¼ 0.05) Constant 63.9286 X1 4.3792 X2 6.5042 X3 7.6208 X4 4.4625 X12 1.3564 X22 1.7189 X32 1.3189 X42 3.4811 X1 * X2 2.0938 X1 * X3 0.3312 X1 * X4 0.4437 X2 * X3 2.1062 X2 * X4 0.6938 X3 * X4 0.4313 1.1299 56.580 0.6102 7.177 0.6102 10.659 0.6102 7.313 0.6102 12.489 0.5590 2.426 0.5590 3.705 0.5590 2.359 0.5590 6.227 0.7473 2.802 0.7473 0.443 0.7473 0.594 0.7473 2.818 0.7473 0.928 0.7473 0.577 no longer occurred because of the saturation miscibility of su- percritical methanol in the oil phase at a given temperature and pressure. The response plot of FAME yield incorporating the interaction between reaction time (X2) and temperature (X3) is given in Fig. 3C. From this figure, it can be observed a slight increase in the methyl ester yield at the lowest temperature (250 C) and shortest reaction time (120 s) regardless the change in levels of another parameter. When the temperature is ramped to 350 C, the yield of methyl 0.000 ester increases almost linearly at longer reaction time and vice- 0.000 versa. The resulting response plot shows conformity with experi- 0.000 0.000 mental results in Fig. 2b and may reveal that the thermal degra- 0.000 dation of fatty acid methyl esters in the mixture has not occurred at 0.027 temperature of 350 C for reaction time of 120e600 s. From the 0.007 previous studies [36,37], it can be concluded that the extent of 0.031 0.000 thermal degradation of methyl esters in the mixture is typically 0.013 controlled by reaction time and

temperature in the process. For 0.664 example, methyl palmitate and methyl oleate remain stable at 0.561 350 C for reaction time up to 20 min and 90 min, respectively 0.012 while methyl linoleate started to gradually decompose when 0.367 0.572 reaction time was longer than 20 min for the same reaction temperature [36,37]. The response plots of

16**FAME yield as a function of** pressure (X1) and **methanol** to **oil molar ratio** (X4) **and**

temperature (X3) and

26**methanol to oil molar ratio** (X4) are presented **in** Fig. 3E **and**

F, respectively. In these figures, it can be seen higher significance level of

8**methanol to oil molar ratio** than pressure **and temperature** in maximizing **the**

response. Another observation is the methyl ester yield tends to slightly increase and then remains nearly constant in the curve area of methanol/oil molar ratio between 0 (25:1) and 2 (35:1) in each pressure and temperature level, reflecting saturation miscibility of supercritical methanol in the oil at this condition. This observation is in conformance with experimental results in Fig. 2a. Finally, the two-parameter interaction between pressure (X1) and temperature (X3) toward FAME yield is illustrated in Fig. 3D. It can be seen that increasing temperature and pressure at a constant

7**methanol to oil** feed **ratio and reaction time** led **to**

the increase in FAME yield. This may be attributed to the increasing homogeneity of methanol/oil mixture as a result of the enhanced solvent density and miscibility of supercritical methanol in the oil phase at elevated pressure and temperature. The profiles of FAME yield with the optimized reaction pa- rameters are shown in Fig. 4. In this figure, it can be seen the contribution of each parameter involved in the supercritical methanol transesterification of KSO with significance level against FAME yield in the order of

23**methanol to oil molar ratio** (X4) >**reaction time** (X2) >**pressure**

(X1) > temperature (X3). The curve profiles of pressure, reaction time, and temperature show similar trends in which FAME yield increases exponentially along the curvature line. The curve profile of methanol to oil molar ratio also indicates a positive effect toward FAME

27**yield up to a certain point and** then **the yield**

of the product remains nearly constant at higher molar ratio. The optimum reaction conditions for super-critical methanol transesterification of KSO are as follows:

6**methanol to oil molar ratio of** 30 **:1; temperature of** 322 **C;** pressure **of**

16.7 MPa; and reaction time of 476 s with calculated response (FAME yield) of 95.5%. This response value was validated by triplicate experiments under the above optimum condition and it was found an insignificant error of 0.3% between experimental and the calculated response. For comparison purpose, several statistical studies and the optimized reaction parameters for the Table 4 A summary of several statistical studies and the optimized reaction conditions for catalyst-free biodiesel production. Reaction mixture Reactor Optimized conditions type Alcohol/oilb T (C) P FAME R2adj Time yield (%) (MPa) (min) Refined palm oil þ SCEa [18] Refined palm oil þ SCMa [20] Wet algae paste þ SCM [21] Refined PKOd þ SCM [22] Batch Batch Batch Plug flow Radish oil þ SCM [38] Radish oil þ SCE [38] Batch Rapeseed oil þ SCM [39] Batch Rapeseed Batch oil þ SDMCa [40] Kapok Batch oil þ SCM [this study] 33:1 349 40:1 372 9:1 255 42:1 325 39:1 39:1 317 319 50:1 42:1 330 300 30:1 322 ndc 30 nd 16 nd 25 18 nd nd nd 27 22 21 20 16 20 16.7 7.9 79.20 0.97 81.50 0.96 85.02 0.92 93.70 0.92 97.00 0.99 97.50 0.92 93.60 0.96 97.40 e 95.50 0.94 a SCM (supercritical methanol); SCE (supercritical ethanol); SDMC (supercritical dimethyl carbonate). b The unit is molar ratio, otherwise specified (the unit of alcohol to oil ratio in Ref. [21] is wt/vol). c Not determined. d Palm kernel oil. catalyst-free biodiesel production reported by several authors are summarized in Table 4. Actually, it can be seen that there is no definite trend or combination of the optimized reaction parame- ters toward FAME yield for supercritical transesterification pro- cess using different kinds of oil feedstocks. By comparing the statistical analysis results that incorporate four reaction parame- ters simultaneously between the present work and those obtained by Shin et al. [39] and Ilham and Saka [40], the optimized pressure and temperature are both comparable. However, the optimized values of methanol to oil molar ratio and reaction time in this work are lower than those reported by Shin et al. [39] and Ilham and Saka [40] for obtaining FAME yield higher than 90%. There- fore, the optimized supercritical transesterification conditions in Fig. 4. Profiles of FAME yield with the optimized reaction parameters (D ¼ composite desirability; y ¼ calculated FAME yield; d ¼ desirability). Table 5 Properties of biodiesel derived from kapok oil (KSO) and C. oleifera Abel oil [42] and its comparison with petro-diesel fuel. Fuel properties Feedstock C. oleifera Abel oil KSO ASTM D6751 Diesel fuel (ASTM D975) Cetane index Flash

36**point (C)** Pour **point (C) Acid value (mg KOH/g)** Relative **density Kinematic viscosity** (mm2/s) **at 40 C e**

57 150 154 e 0 0.22 0.19 e 0.88 4.54 4.3 48e65 100e170 15 to 10 max 0.5 0.87e0.9 1.9e6 38e55 60e80 35 to 15 e 0.85 1.3e5.5 this work are considered more efficient and economically viable for industrial practice than the two reported studies. 3.3. Fuel properties of KSO-derived

20**biodiesel The fuel properties of** KSO-derived **biodiesel are** summarized **in Table 5.**

As shown in this table, all fuel properties of biodiesel met the standard specifications according to ASTM D6751. The obtained results were also compared with the fuel properties of petro-diesel as specified in ASTM D975 [41] and biodiesel prepared from C. oleifera Abel oil [42]. The flash point (or autoignition tempera- ture) of KSO-biodiesel is twice higher than that of petro-diesel fuel,

25**indicating safer handling and storage** for **this fuel in high** temper- ature **environment.**

Another crucial property of biodiesel that related to the engine performance is kinematic viscosity, characterizing the extent of fluidization and atomization of the fuel when used at low temperature. The kinematic viscosity of KSO-biodiesel is comparable to that of petro-diesel fuel thus ensuring its suit- ability to be used in the conventional diesel engines without extensive modifications. A higher cetane index of biodiesel reveals better ignition quality with shorter delay time compared to petro-diesel thereby a more efficient engine performance. In addition, the engine emissions produced from the combustion of biodiesel contain less soot par- ticles than that generated from petro-diesel due to the presence of ester- and/or ether-based oxygenated compounds [35]. The acid value of biodiesel was lower than petro-diesel, representing greater oxidative and thermal stabilities and also longer shelf time of this fuel during transportation and storage. Lower acid value in bio- diesel may be due to esterification reaction of free fatty acids into fatty acid methyl esters and water during supercritical trans- esterification process. The cold flow characteristic of biodiesel is designated as pour point and it was found to be 0 C for KSO- biodiesel. This value is in conformance with ASTM D6751 and ASTM D975 specifications and can be further lowered by the addition of fuel additives or blending with diesel oil. Compared with fuel properties of biodiesel derived from C. oleifera Abel oil, KSO-biodiesel possesses similar characteristics in terms of kine- matic viscosity and flash point, possibly due to similarity in the composition of the fuel that comprise the majority of unsaturated fatty acid methyl esters such as methyl oleate and methyl linoleate. 4. Conclusions The non-catalytic production of biodiesel from non-edible and underutilized kapok oil (KSO) via supercritical methanol trans- esterification has been conducted in this work. Response surface methodology (RSM) and four-way ANOVA have been successfully applied for designing and optimizing the experiments with respect to methanol to oil molar ratio, pressure, temperature, and reaction time. The optimum reaction conditions for the supercritical methanol transesterification of KSO to biodiesel are as follows:

6**methanol to oil molar ratio of** 30 **:1, temperature of** 322 **C,** pressure **of**

16.7 MPa, and reaction time of 476 s with FAME yield of 95.5%. The quadratic polynomial regression model gave a good fit toward experimental results with the adjusted coefficient of determination ðR2adjÞ close to unity (0.94). The profiles of FAME yield with opti- mized reaction parameters show the significance level of the parameters toward the response in the order of

20**methanol to oil molar ratio > reaction time**> pressure >**temperature, which**

conforms the experimental results. The fuel

12**properties of biodiesel** prepared **from** kapok **oil** are **in** conformance **with**

ASTM D6751 standard specifications. Acknowledgments This project is supported by the Australian Research Council (ARC) through the ARC Future Fellowship Program (FT100100879). References [1] Siddiquee MN, Rohani S. Lipid extraction and biodiesel production from municipal sewage sludges: a review. Renew Sustain Energ Rev 2011;15: 1067e72. [2] Wellert S, Karg M, Imhof H, Steppin A, Altmann HJ, Dolle M, et al. Structure of biodiesel based bicontinuous microemulsions for environmentally compatible decontamination: a small angle neutron scattering and freeze fracture electron microscopy study. J Colloid Interf Sci 2008;325:250e8. [3] Pramanik K. Properties and use of jatropha curcas oil and diesel fuel blends in compression ignition engine. Renew Energy 2003;28:239e48. [4] Canakci M, Ozsezen AN, Arcaklioglu E, Erdil A. Prediction of performance and exhaust emissions of a diesel engine fueled with biodiesel produced from waste frying palm oil. Expert Syst Appl 2009;36:9268e80. [5] Ma F, Hanna MA. Biodiesel production: a review. Bioresour Technol 1999;70: 1e15. [6] Endalew AK, Kiros Y, Zanzi R. Heterogeneous catalysis for biodiesel production from Jatropha curcas oil (JCO). Energy 2011;36:2693e700. [7] Jain S, Sharma MP. Kinetics of acid base catalyzed transesterification of Jatropha curcas oil. Bioresour Technol 2010;101:7701e6. [8] Meng X, Chen G, Wang Y. Biodiesel production from waste cooking oil via alkali catalyst and its engine test. Fuel Process Technol 2008;89:851e7. [9] Peng-Lim B, Ganesan S, Maniam GP, Khairuddean M. Sequential conversion of high free fatty acid oils into biodiesel using a new catalyst system. Energy 2012;46:132e9. [10] Uzun BB, Kilic M, Ozbay N, Putun AE, Putun E. Biodiesel production from waste frying oils: optimization of reaction parameters and determination of fuel properties. Energy 2012;44:347e51. [11] Shin HY, Lee SH, Ryu JH, Bae SY. Biodiesel production from waste lard using supercritical methanol. J Supercrit Fluid 2012;61:134e8. [12] Demirbas A. Biodiesel production via non-catalytic SCF method and biodiesel fuel characteristics. Energy Convers Manage 2006;47:2271e82. [13] Supranto. The biodiesel production process from vegetable oil. Dev Chem Eng Min Process 2005;13:687e92. [14] Sivakumar P, Sindhanaiselvan S, Gandhi NN, Devi SS, Renganathan S. Optimization and kinetic studies on biodiesel production from underutilized Ceiba pentandra oil. Fuel 2013;103:693e8. [15] Minami E, Saka S. Kinetics of hydrolysis and methyl esterification for bio- diesel production in two-step supercritical methanol process. Fuel 2006;85: 2479e83. [16] Kusdiana D, Saka S. Two-step preparation for catalyst-free biodiesel fuel production: hydrolysis and methyl esterification. Appl Biochem Biotechnol 2004;113e116:781e91. [17] Ilham Z, Saka S. Two-step supercritical dimethyl carbonate method for biodiesel production from Jatropha curcas oil. Bioresour Technol 2010;101: 2735e40. [18] Gui MM, Lee KT, Bhatia S. Supercritical ethanol technology for the production of biodiesel: process optimization studies. J Supercrit Fluid 2009;49:286e92. [19] Tan KT, Lee KT, Mohamed AR. Production of FAME by palm oil trans- esterification via supercritical methanol technology. Biomass Bioenergy 2009;33:1096e9. [20] Tan KT, Gui MM, Lee KT, Mohamed AR. An optimized study of methanol and ethanol in supercritical alcohol technology for biodiesel production. J Supercrit Fluid 2010;53:82e7. [21] Patil PD, Gude VG, Mannarswamy A, Deng S, Cooke P, Munson-McGee S, et al. Optimization of direct conversion of wet algae to biodiesel under supercritical methanol conditions. Bioresour Technol 2011;102:118e22. [22] Sawangkeaw R, Bunyakiat K, Ngamprasertsith S. Continuous production of biodiesel with supercritical methanol: optimization of a scale-up plug flow reactor by response surface methodology. Fuel Process Technol 2011;92: 2285e92. [23] ASTM D5555-95. Standard test method for determination of free fatty acids contained in animal, marine, and vegetable fats and oils used in fat liquors and stuffing compounds. http://www.astm.org/Standards/D5555.htm; 2011. [24] ASTM D6751-12. Standard specification for biodiesel fuel blend stock (B100) for middle distillate fuels. http://www.astm.org/Standards/D6751.htm. [25] ASTM D613-10a. Standard test method for cetane number of diesel fuel oil.

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